

# RECOVERY OF IRON FROM LOW-GRADE HEMATITE ORE USING COAL-BASED DIRECT REDUCTION FOLLOWED BY MAGNETIC SEPARATION

N. Alavi Fard, H. Shalchian\*, A. Rafsanjani-Abbasi, J. Vahdati Khaki and A. Babakhani

\* h.shalchian@stu.um.ac.ir

Received: June 2015

Accepted: August 2016

Iron and Steel Research Center, Department of Materials Science and Metallurgical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran.

**Abstract:** In the present work, iron recovery from a low-grade hematite ore (containing less than 40% iron), which is not applicable in common methods of ironmaking, was studied. Non-coking coal was used as reducing agent. Reduction experiments were performed under various coal to hematite ratios and temperatures. Reduction degree was calculated using the gravimetric method. Reduced samples were subjected to magnetic separation followed by X-ray diffraction analysis. Total iron content, degree of metallization and recovery efficiency in magnetic part were determined by quantitative chemical analysis, which were obtained about 82%, 95% and 64% respectively under optimal conditions. CaO as an additive improved ore reducibility and separation efficiency. The microstructure of reduced samples and final products were analyzed by scanning electron microscopy. Final product with a high degree of metallization can be used in steel making furnaces and charging of blast furnaces which can improve production efficiency and decrease coke usage.

**Keywords:** Low-Grade Iron Ore, Coal-Based Direct Reduction, Sponge Iron; Lime, Magnetic Separation.

## 1. INTRODUCTION

In recent years, global demand for iron ore and its cost is highly increasing due to the improvement of the overall technical level in the steel industry [1]. With the continuous exhaustion of mineral resources, iron ore deposits become increasingly scarce. Hence, main global iron and steel producers would try to replace their failing high-grade mines with new sources of iron and decrease the cost of final product [2]. In this regard, researchers have conducted numerous studies on the use of secondary sources of iron. One such example is the recovery of iron from cyanide tailings with reduction roasting–water leaching followed by magnetic separation in which the iron grade of magnetic concentrate of 59.11% and the recovery ratio of 75.12% were obtained [3]. Another example is the method of magnetizing roasting-magnetic separation for iron recovery from red mud and iron ore tailings [2-4]. In some other studies, instead of magnetizing roasting, sponge iron was directly produced from pyrite cinder [3, 4], red mud [5,6], and other tailings. For example, a magnetic concentrate containing 90.31% total iron and

89.76% metallization with a total iron recovery rate of 83.88% was obtained after 60 min reduction roasting of vanadium tailings at 1200°C [4].

Magnetic separation is applied after direct reduction to obtain sponge iron in all of these studies. Magnetic separation is a method to separate and capture fine magnetic particles by the magnetic force acting on the particles in a gradient magnetic field [7].

Solid tailings containing iron usually have a high content of impurities such as SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and complex chemical and mineralogical compositions [2, 3] which causes a difficult separation process. Therefore, it is difficult to obtain a high-grade iron product directly using traditional mineral processing techniques [3,4]. It is well known that the magnetizing roasting or direct reduction-magnetic separation is an effective method for iron recovery from solid tailings [2-6].

Low-grade iron ores are also another example that can be considered as a new source of iron. The recovery of iron from low-grade iron ores has been investigated by many researchers using froth flotation process [8], reverse anionic

flotation of quartz [9], and magnetic separation [10].

In this research, recovery of iron in coal-based direct reduction - magnetic separation method is studied. The iron ore was collected from a low-cost low-grade high silica iron reservoir as a new source of iron and also non-coking coal was used as reducing agent. After evaluating reduction parameters for iron recovery, the effect of lime on the efficiency of magnetic separation was studied. This study demonstrated that the method of coal-based direct reduction - magnetic separation is an effective technique to recover

iron from low-grade iron ores. The highly metalized final product can be used in steel making and charging of blast furnaces.

## 2. MATERIALS AND METHODS

### 2. 1. Raw Materials

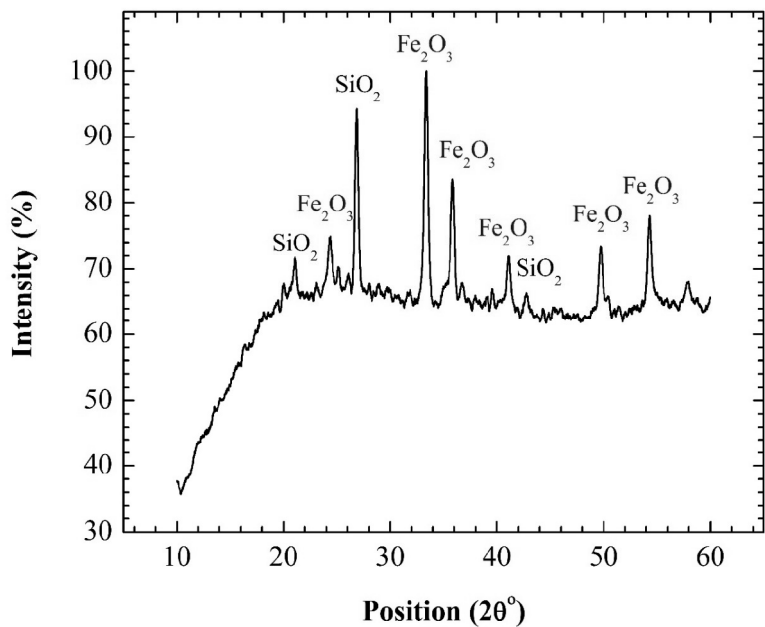
A low-grade iron ore was collected from an Iranian mine (Neyshabour, Khorasan Razavi province) and was used for experiments. Ores were sampled and sieved through 100 mesh screen. Phase detection and chemical analysis of

**Table 1.** Chemical composition of low-grade iron ore

| Components     | Fe <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | TiO <sub>2</sub> | CaO  | MgO  | MnO  | Na <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | LOI   |
|----------------|--------------------------------|------------------|--------------------------------|------------------|------------------|------|------|------|-------------------|-------------------------------|-------|
| Content (Wt.%) | 47.14                          | 28.1             | 7.58                           | 2.16             | 0.64             | 0.51 | 0.37 | 0.06 | 0.06              | 0.1                           | 13.28 |

**Table 2.** Proximate analysis of coal

| Components     | Fixed carbon | Volatile matter | Ash | Moisture |
|----------------|--------------|-----------------|-----|----------|
| Content (Wt.%) | 84           | 6               | 7   | 3        |



**Fig. 1.** XRD pattern of low-grade iron ore.

the powder were done using X-ray diffraction (XRD) analyzer (Philips PW1800) and X-ray fluorescence (XRF) spectroscopy (Philips PW1480). Quartz and hematite were detected as the main phases exist in the ore (Fig. 1). The chemical composition of iron ore is listed in Table 1.

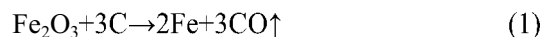
In addition, SEM image of this powder and its EDS analysis are shown in Fig. 2.

In reduction process, non-coking coal was used as a reducing agent and its approximate composition are in Table 2. Analytical grade lime was used in final experiments.

## 2. 2. Experimental Procedure

Reduction experiments were performed in two main groups. Parametric studies were carried out firstly, to clarify the effects of temperature, reaction time and coal/hematite ratio on reduction process. Afterward, some other experiments were done in presence of lime to study the effect of lime on separation efficiency.

It is known that the predominance mechanism in coal-based direct reduction is considered as following equation:



Thus, the required stoichiometric carbon for direct reduction process can be estimated considering iron ore analysis (table 1) and equation 1.

A homogeneous mixture of iron ore and coal which was prepared under desired ratios, was subjected to reduction experiments. An alumina crucible with gas escape vents was used. It was completely covered with charcoal to prevent re-oxidation in reduction and cooling stages by making a reductive atmosphere which diminishes oxygen content of the electric furnace chamber. As a result, this simple procedure can considerably prevent the oxygen penetration from the outer atmosphere to the reaction container.

Reduction degree of samples was calculated using equation 2 based on gravimetric method:

Afterward, the sample which was reduced under optimal conditions of temperature, reaction time and coal/hematite ratio was magnetically separated (manual separation) and subjected to X-ray analysis. Finally, total iron content, degree

$$\text{Reduction degree (\%)} = \frac{\text{Experimental weight loss}}{\text{Theoretical weight loss } [\text{CO} + (\text{moisture} + \text{LOI} + \text{volatile matter})_{\text{coal+ore}}]} \quad (2)$$

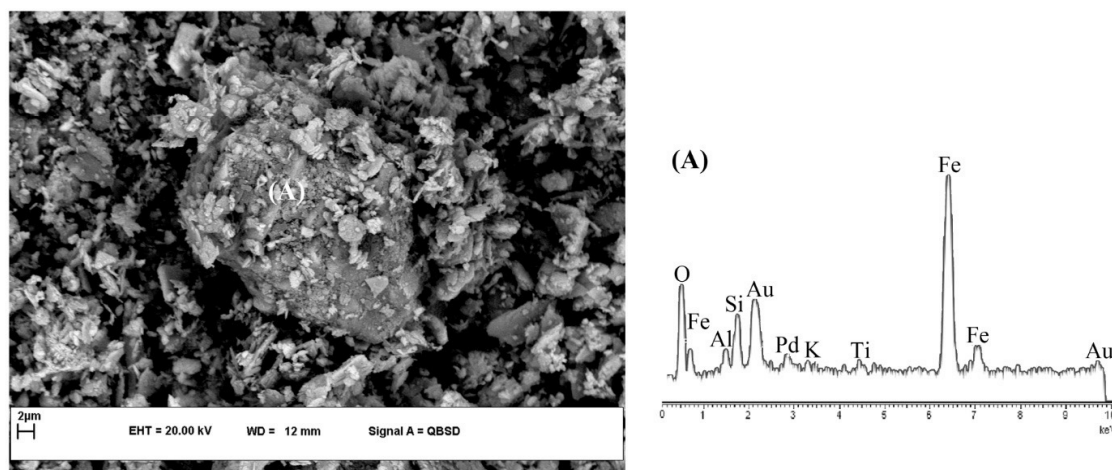


Fig. 2. SEM image of low-grade hematite ore and its EDS analysis at (A) area.

of metallization in magnetic part and recovery efficiency were determined by standard quantitative chemical analysis.

### 3. RESULTS AND DISCUSSION

#### 3. 1. Effect of Temperature and Time on Reduction Degree

Several experiments were carried out to determine the effect of temperature and time on reduction process. Fig. 3 is a plot of reduction degree at different temperatures (950°C, 1000°C and 1050°C) as a function of reaction time. The ratio of coal/hematite was kept constant equal to 125% of stoichiometry value of required coal to obtain complete hematite reduction. As expected, the results in Fig. 3 showed that reduction degree has increased by increasing temperature and reaction time. It is evident from Fig. 3 that reduction has mainly occurred at the first hour and then has reached to an almost constant value after 3 hours. Temperature increment from 950°C to 1050°C has increased reduction degree about

20-25%. Therefore, temperature has a considerable effect on reduction and improves the reactions kinetic. So, it can be considered as the main factor that affects the reduction reaction [2].

#### 3. 2. Effect of Amount of Coal on Reduction Degree

Different ratios of coal/hematite were examined to investigate the effect of coal amount on progress of reduction reaction. These series of experiments were performed at 1050°C for 3 hours. Reduction degree calculations for different values of coal are given in Table 3. The results which are presented in Fig. 4 reveal that at a constant temperature and time, reduction degree has increased by increasing the coal/hematite ratios. Coal/hematite ratio increment improves total active surfaces between hematite and coal particles, accelerating coal gasification reaction. The more gasification reaction proceeds, the more CO formation occurs, resulting in more reduction degree. However, it should be noted that the coal value has less effect on reduction



Fig. 3. Effect of reaction time and temperature on reduction degree at a constant ratio of coal/hematite (125% of stoichiometry value of required coal for complete hematite reduction).

**Table 3.** Calculations of reduction degree for different values of coal

| Ore (g) | Stoichiometric coefficient of required coal | Coal (g) | Coal (Wt. %) | Moisture and Volatile matter(g) | Theoretical CO (g) | LOI (g) | Theoretical weight loss (g) | Experimental weight loss (g) | Reduction Degree% |
|---------|---------------------------------------------|----------|--------------|---------------------------------|--------------------|---------|-----------------------------|------------------------------|-------------------|
| 10      | 1.05                                        | 1.32     | 11.66        | 0.12                            | 2.47               | 1.33    | 3.92                        | 3.57                         | 91.07             |
| 10      | 1.25                                        | 1.57     | 13.57        | 0.14                            | 2.47               | 1.33    | 3.94                        | 3.63                         | 92.13             |
| 10      | 1.50                                        | 1.89     | 15.90        | 0.17                            | 2.47               | 1.33    | 3.97                        | 3.77                         | 94.96             |
| 10      | 1.75                                        | 2.20     | 18.03        | 0.20                            | 2.47               | 1.33    | 4.00                        | 3.84                         | 96.00             |
| 10      | 2.00                                        | 2.52     | 20.13        | 0.23                            | 2.47               | 1.33    | 4.03                        | 3.91                         | 97.02             |

**Fig. 4.** Effect of coal weight percent on reduction degree at 1050°C for 3 hours.

degree, because by doubling the coal / hematite ratio, reduction degree has increased only about 6%.

Considering all experiments in various conditions, to obtain maximum reduction degree, the optimal levels of temperature, reaction time and coal/hematite ratio are 1050 °C, 4 hours and 125% of stoichiometry value, respectively. It should be mentioned that, although 200% of stoichiometry value of coal/hematite ratio has resulted in higher reduction degree, but much more coal should be used to increase only 5% in reduction degree and it can make the process economically inefficient.

### 3. 3. XRD Analysis of Reduced Ore

The reduced sample under the optimal conditions, with 96% reduction degree, was subjected to X-ray diffraction analysis and the result is shown in Fig. 5a. This result is in agreement with gravimetric calculations. As shown, no traces of iron oxides were observed in this pattern, indicating complete hematite reduction and highly metalized sponge iron production. However, high amounts of gangue still exist in the final product. According to Table 1 and reduction calculations, final reduced sample contains 55% gangue and 45% Fe. This amount of gangue, mainly consist of silica, makes the obtained sponge iron useless in

steelmaking furnaces. Thus, it is necessary to diminish most of the gangue to gain a high-grade sponge iron product. It is well known that magnetic separation is an effective method for iron recovery from solid tailings [2-6]. Therefore, this method was applied for iron concentrating.

### 3. 4. Magnetic Separation and Quantitative Chemical Analysis

In this step, two groups of experiments were performed: one in presence and the other in the absence of lime:

#### 3. 4. 1. Magnetic Separation of Reduced Sample in the Absence of Lime

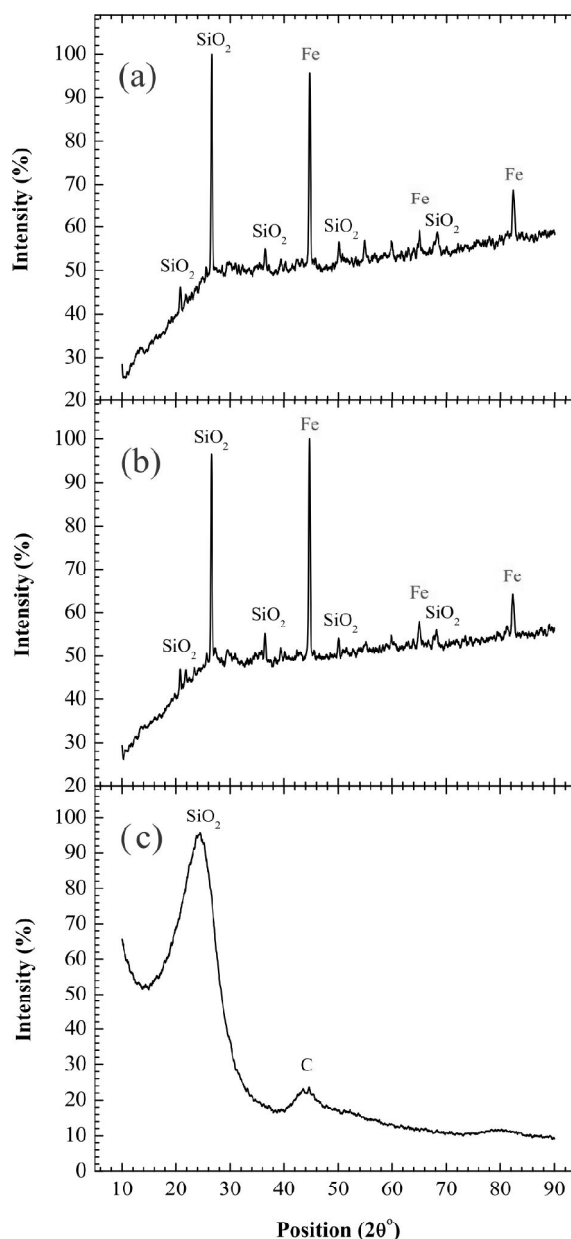
The reduced sample under the optimal conditions was magnetically separated and each part was subjected to X-ray diffraction analysis. XRD patterns are presented in Fig. 5b and Fig. 5c. Quantitative chemical analysis results showed that a magnetic concentrate with 98% recovery efficiency and 50% total Fe was obtained. It is clear that the separation efficiency was not acceptable. Because there is still quartz's peak in the diffraction pattern of magnetic part. Also, there is no characteristic peak in the diffraction pattern of the non-magnetic part, which indicates the absence of quartz in this part. Complex dissemination characteristics of reduced samples could be the reason for low separation efficiency of gangue from iron [2,3].

#### 3. 4. 2. Magnetic Separation of Reduced Sample in Presence of Lime

Reduction experiments in presence of lime were carried out at 1050°C for an hour at different weight ratios of lime/(ore + coal) (Table 4). The results were remarkable and reduction degree increased significantly in presence of lime (Fig. 6). Therefore, with addition of lime (only 9% of total weight of iron ore and coal mixture) 96% reduction degree was achieved in 1 hour. In other words, the lime has improved the reducibility of the low-grade iron ore.

The ore properties such as particle size, density, porosity, composition and crystal structure determine its reducibility and some additives such

as alkali oxides and carbonates can affect it [11-14]. This result is consistent with a literature report that presence of CaO in the charge mix of pellets



**Fig. 5.** XRD patterns of the sample with maximum reduction degree (96%), reduced under optimal conditions (1050°C, 3hours, 125% of stoichiometry value of required coal for complete hematite reduction). (a) Before magnetic separation, (b) Magnetic part and (c) Non-magnetic part after separation.

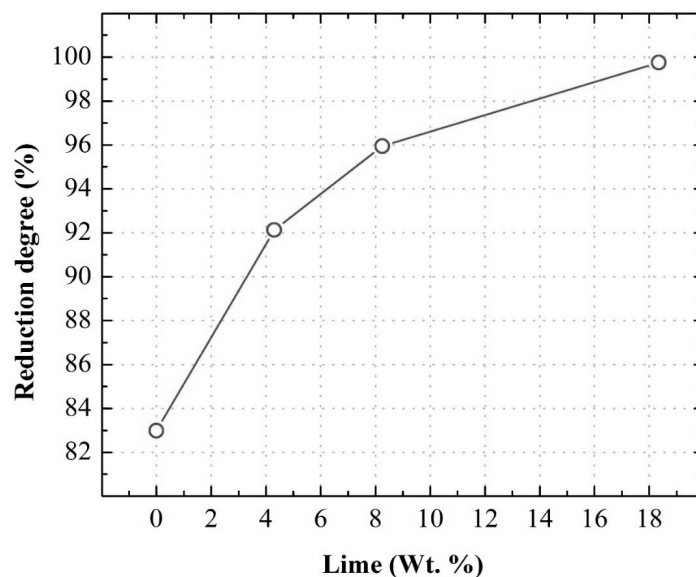


Fig. 6. Effect of lime weight percent on reduction degree at 1050°C for 1 hour.

Table 4. Calculations of different values of lime and reduction degree

| Ore (g) | Coal (g) | Lime ratio to (coal+ore) mixture (%) | Weight of Lime (g) | Weight percent of Lime (%) | Theoretical weight loss (g) | Experimental weight loss (g) | Reduction Degree% |
|---------|----------|--------------------------------------|--------------------|----------------------------|-----------------------------|------------------------------|-------------------|
| 10      | 1.57     | 0                                    | 0                  | 0                          | 3.94                        | 3.27                         | 82.99             |
| 10      | 1.57     | 4.5                                  | 0.52               | 4.30                       | 3.94                        | 3.63                         | 92.13             |
| 10      | 1.57     | 9                                    | 1.04               | 8.25                       | 3.94                        | 3.78                         | 95.94             |
| 10      | 1.57     | 22.5                                 | 2.60               | 18.35                      | 3.94                        | 3.93                         | 99.75             |

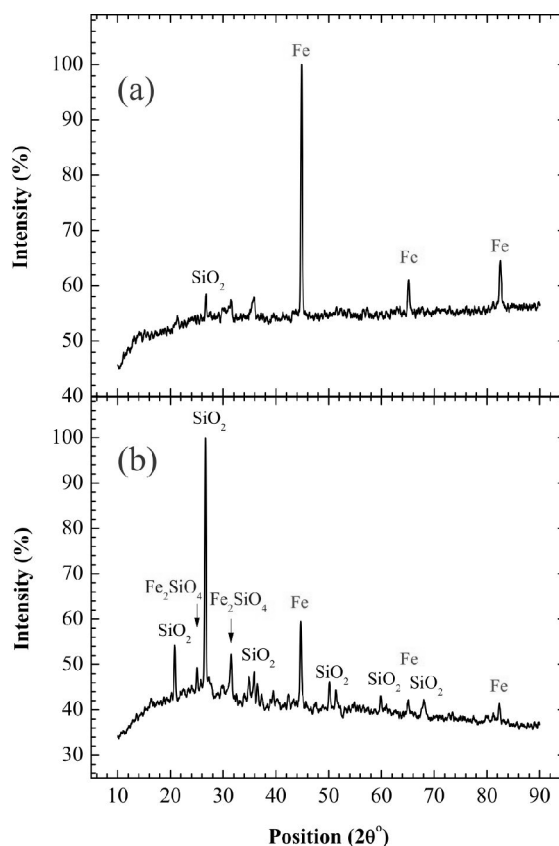
increases the reducibility of iron ore [12]. CaO additive promoting gasification reaction as an alkali catalyst and mechanism of alkali gasification is not well understood [12, 13]. It is also reported that presence of alkalis increases iron ore cracking and swelling during reduction, therefore improving mass transfer in reaction, which results in higher reducibility of iron oxide [12, 15].

With this in mind, the new optimal conditions for temperature, reaction time, coal/hematite and lime/(ore + coal) ratios are as follows: 1050°C, 1 hour, 125% of stoichiometry value of required coal/hematite and 9% of total weight of iron ore and coal mixture, respectively. Under these

conditions, according to equation (2), the reduction degree of 96% was gained. The sample was then magnetically separated and X-ray diffraction patterns of magnetic and non-magnetic parts were obtained (Fig. 7). The quartz's peak has disappeared considerably in magnetic part of Fig. 7a in comparison with Fig. 5b due to aforementioned lime effect.

Presence of quartz's peak in the diffraction pattern of non-magnetic part (Fig. 7b) proves higher separation efficiency, which was not seen in Fig. 5c.

CaO addition, which enhanced the ore reducibility, is the reason for higher separation efficiency. As it mentioned above, presence of



**Fig. 7.** XRD patterns of the sample with maximum reduction degree (96%), reduced under final optimal conditions (1050°C, 1hour, 9%lime, 125% of stoichiometry value of required coal for complete hematite reduction). (a) Magnetic part and (b) Non-magnetic part after magnetic separation.

alkalis increases iron ore cracking during reduction. Therefore, it is expected that CaO reacts with silica acidic oxide to form calcium silicates. The cracking occurs during reduction reaction can improve liberation degree of iron from silica particles and consequently, leads to a more efficient separation.

The XRD pattern of non-magnetic part (Fig. 7b) also shows the presence of  $\text{Fe}_2\text{SiO}_4$  which is the product of a reaction between FeO and  $\text{SiO}_2$ . In other words, there are still some iron oxide that has not been reduced to iron and can participate in a reaction with  $\text{SiO}_2$ . It should be mentioned that the formation of  $\text{Fe}_2\text{SiO}_4$  has no effect on the amount of stoichiometric carbon required for complete reduction.

The amount of carbon has been calculated for complete reduction, which is an ideal state, but some iron oxide would be remained without

complete reduction in real situations. Hence there are still some residual carbon at the end of reduction duration. On the other hands, the results showed that the coal value has less effect on reduction degree. Therefore, the residual carbon does not affect neither stoichiometric carbon calculations nor the reduction process.

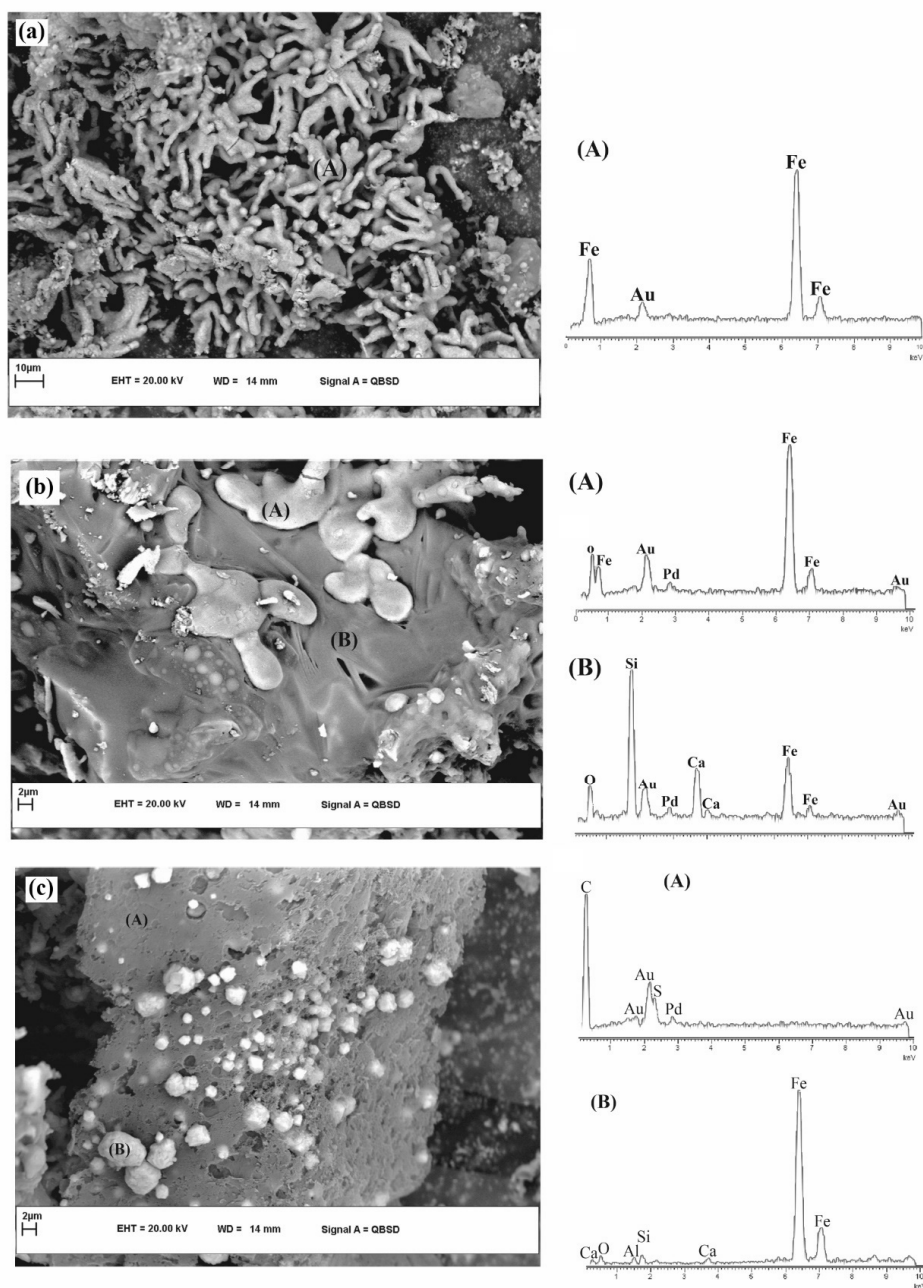
### 3. 5. SEM-EDS Analysis of Reduced Sample in Presence of Lime

The SEM images of reduced sample under optimal conditions are shown in Fig. 8. SEM observations showed that, three types of main particles exist in reduced sample. The first type has sponge-like morphology and its EDS analysis revealed that it is sponge iron. Fig. 8a shows these iron clusters.

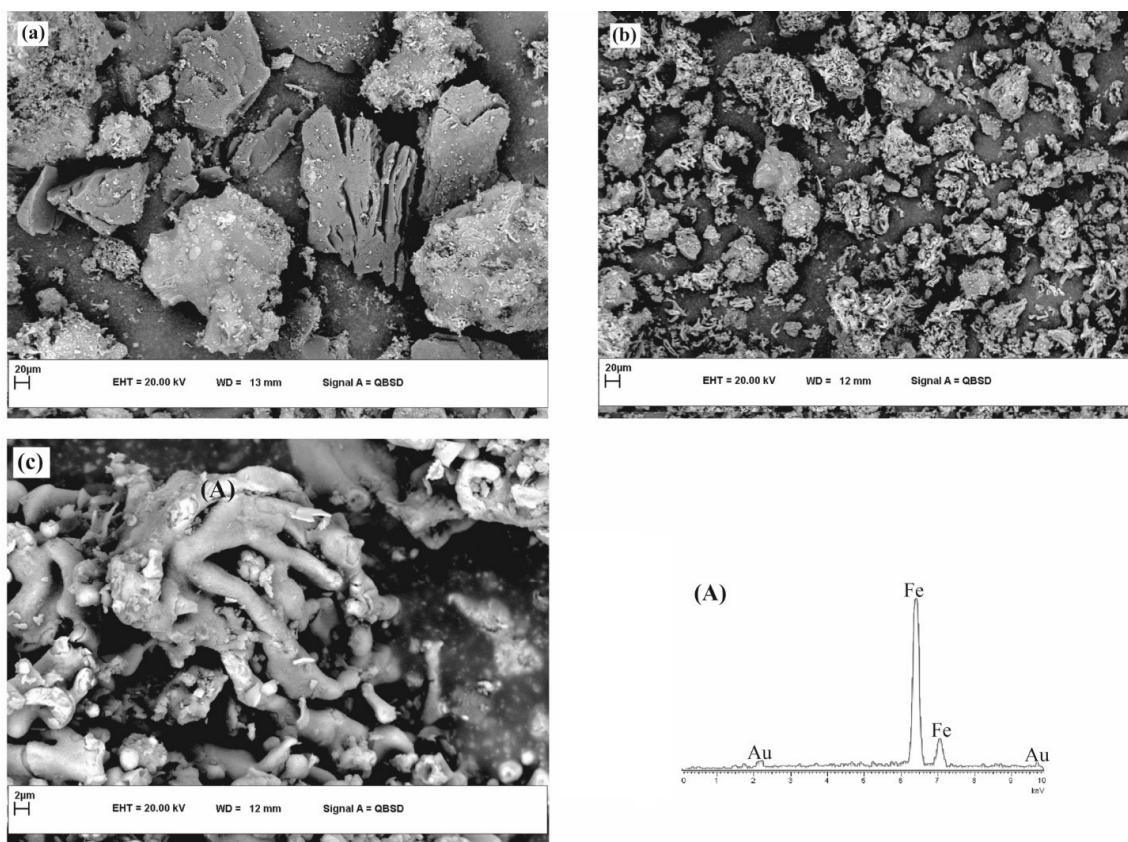
The second type has irregular morphology and

EDS analysis showed that they are gangue with iron particles on their surfaces (Fig. 8b). The main constituent in the base particle is silica, whereas bright areas on the surface are iron. The EDS analysis showing CaO incorporated in silica

that can improves liberation of iron particles. Hence, CaO was not detected in XRD patterns. Besides its low amount (about 8wt.%), it has incorporated with silica in a range of compositions and does not have any specific



**Fig. 8.** SEM images of reduced sample in presence of lime: (a) The first type morphology (sponge iron), (b) The second type morphology (gangue particles), (c) The third type morphology (residual coal particles), with their EDS analysis at corresponding (A) and (B) areas.



**Fig. 9.** SEM images of magnetic and non-magnetic parts: (a) non-magnetic part, (b) magnetic part, (c) an iron cluster of magnetic part and its EDS analysis at (A) area.

significant diffraction peak.

Eventually, decorated gray coal particles with bright iron spots in their porosity have formed the third type of morphology in SEM image (Fig. 8c). This figure indicates penetration of iron particles to coal during reduction of hematite particles on the surface of coal.

Based on these observations, it can be concluded that iron recovery from the second and third type of particles is difficult, but the first type sponge-like iron clusters can be recovered easily by the magnetic separation process.

Fig. 9 shows SEM images of magnetic and non-magnetic parts. As seen in Fig. 9a, the non-magnetic part includes second and third type particles were discussed above, which are coal and gangue with iron particles on their surfaces. The existence of iron particles in non-magnetic

part reduces recovery efficiency in the separation process.

From Fig. 9b it can be seen that sponge iron clusters and some gangue particles present in magnetic product. The superficial iron content of gangue has brought these impurities to the final product during magnetic separation and resulted in decreasing of total iron content of final product. These observations are in agreement with X-ray diffraction patterns and quantitative chemical analysis results. Therefore, SEM-EDS analysis showed the reason of relatively low recovery efficiency and total iron content of the final product.

Finally, the magnetic product was analyzed chemically and results are as follows: total iron content of 82%, degree of metallization of 95% and recovery efficiency ((weight of Fe in

magnetic product/ weight of Fe in low-grade iron ore)  $\times 100$ ) of 64%. Therefore, iron content has increased considerably (from 45% to 82%), which means about 37% decrease in gangue content from a directly reduced complex disseminated low-grade iron ore to a magnetic product.

This product can be used in steel making furnaces and charging of blast furnace which can improve the production efficiency and decrease coke usage because of a high degree of metallization. More studies could be performed to increase total iron content of the final metallic product and achieving high production efficiency.

#### 4. CONCLUSION

A simple method, combined coal-based direct reduction and magnetic separation was developed to recover iron from a low-grade iron ore.

Temperature, reaction time, and the amount of coal and lime have a positive effect on reduction degree. The optimal conditions for temperature, reaction time, coal and lime were obtained as follows: 1050°C, 1 hour, 125% of stoichiometry value of required coal/hematite and 9% of total weight of iron ore and coal mixture, respectively. Under this conditions a product with total iron content, degree of metallization and recovery efficiency of about 82%, 95% and 64% was gained.

CaO as an additive improved ore reducibility and separation efficiency. Iron content has increased considerably (from 45% to 82%) using this simple method, which means about 37% decrease in gangue content of a complex disseminated low-grade iron ore.

The results (degree of metallization and recovery efficiency) demonstrated the feasibility of this simple method for iron recovery from low-grade resources with no commercial value.

#### REFERENCES

1. Guo, Z. and Z. Fu, "Current situation of energy consumption and measures taken for energy saving in the iron and steel industry in China",

- Energy, 2010, 35, 4356-4360.
2. Li, C., Sun, H., Bai, J. and Li, L., "Innovative methodology for comprehensive utilization of iron ore tailings: Part 1. The recovery of iron from iron ore tailings using magnetic separation after magnetizing roasting", Journal of hazardous materials, 2010, 174, 71-77.
3. Zhang, Y., Li, H., and Yu, X., "Recovery of iron from cyanide tailings with reduction roasting–water leaching followed by magnetic separation", Journal of hazardous materials, 2012, 213, 167-174.
4. Yang, H., Jing, L. and Zhang, B., "Recovery of iron from vanadium tailings with coal-based direct reduction followed by magnetic separation", Journal of hazardous materials, 2011, 185, 1405-1411.
5. Li, L., "A study of iron mineral transformation to reduce red mud tailings", Waste management, 2001, 21, 525-534.
6. Liu, W., Yang, J. and Xiao, B., "Application of Bayer red mud for iron recovery and building material production from aluminosilicate residues", Journal of hazardous materials, 2009, 161, 474-478.
7. Satoshi, F., "Magnetic Separation Method for Continuous Separation Process", J. Cryog. Soc. Jpn, 2002, 37, 321-327.
8. Rao, K. H. and Narasimhan, K., "Selective flocculation applied to Barsuan iron ore tailings", International Journal of Mineral Processing, 1985, 14, 67-75.
9. Yuhua, W. and Jianwei, R., "The flotation of quartz from iron minerals with a combined quaternary ammonium salt", International Journal of Mineral Processing, 2005, 77, 116-122.
10. Song, S., Lu, S. and Lopez-Valdivieso, A., "Magnetic separation of hematite and limonite fines as hydrophobic flocs from iron ores", Minerals engineering, 2002, 15, 415-422.
11. Basumallick, A., "Influence of CaO and Na<sub>2</sub>CO<sub>3</sub> as Additive on the Reduction of Hematite-Lignite Mixed Pellets", ISIJ international, 1995, 35, 1050-1053.
12. Biswas, A. K., "Principles of blast furnace ironmaking", SBA publications calcutta, New Delhi, India, 1984.
13. Rao, Y. and Han, H., "Catalysis by alkali

- carbonates of carbothermic reduction of magnetite concentrates”, *Ironmaking Steelmaking*, 1984, 11, 308-318.
14. Ross, H., “A review of problems in iron-ore reduction by solid-state processes”, *Canadian Metallurgical Quarterly*, 1972, 11, 621-628.
  15. Elkasabgy, T., “Effect of alkalis on reduction behavior of acid iron ore pellets”, *Transactions of the Iron and Steel Institute of Japan*, 1984, 24, 612-621.